

# Process for the preparation of viscoplastic polyurethane integral foams showing improved tear strength, elongation at break and tensile strength

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## Abstract of EP 0837093 (A2)

A method for the preparation of tough elastic polyurethane integral foams with improved tear strength, extension at break and tensile strength, comprises reacting optionally modified organic polyisocyanates (A) with at least one high mol.wt. compound (B) containing two or more reactive hydrogen atoms and optionally with low mol.wt. chain extenders and/or cross-linking agents (C), in the presence of catalysts (D), optional propellants (E) and optional auxiliary agents and/or additives (F). At least one recycled polyol obtained by glycolysis of tough elastic polyurethane integral foam using glycidyl ethers is used as (B). Also claimed are tough elastic polyurethane integral foams prepared by the above method.

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The invention relates to a method to the production by tough reading tables polyurethan-integral-foam materials with improved tear strength, elongation at break and tensile strength by conversion of

- a) organic and/or modified organic polyisocyanates also
- b) at least a high-molecular compound with at least two reactive hydrogen atoms and if necessary
- c) low molecular chain extension and/or crosslinking agents
- in presence of
- d) Catalysts,
- e) if necessary blowing agents
- f) as well as if necessary other aids and/or additives.

The invention relates to further after this method prepared tough reading tables of polyurethan-integral-foam materials as well as their use as beer barrel casing.

The production of tough reading tables polyurethan-integral-foam materials by conversion of organic polyisocyanates and/or modified organic polyisocyanates with high-functional compounds with at least two reactive hydrogen atoms and low molecular chain extension and/or crosslinking agents to presence of catalysts, blowing agents, aids and/or additives is known if necessary and became multiple described. A recapitulatory revue over the production from polyurethan-integral-foam materials e.g. becomes. in the plastic handbook, tape VII, "polyurethanes", 1. Edition 1966, edited of Dr. R. Vieweg and Dr. A. Höchtlen, and 3. Edition 1993, edited of Becker/brown one (Carl Hanser publishing house, Munich) given.

It is likewise known that for the production of polyurethane foams of polyols used to become to be able, those for their part from PU wastes by conversion with at least 2 oh group contained compounds, which became so called Glykolyse, obtained. Thus for example DE-A-25 describes 16,863 the production of a polyole mixture from PU wastes and aliphatic diols, which is suitable for the production of polyurethane rigid foam materials. After DE-A-40 24,601 a polyolhaltige dispersion obtained from PU urea wastes by Glykolyse, which can become the production of hard or semihard polyurethanes or PU urea used, becomes. In accordance with US 4.014.809 (DE-A-25 57,172) synthesized polyolhaltige liquid mixtures become as expanded polystyrene component reused from polyurethane rigid foam materials. Polyolhaltige liquids, prepared after DE-A-37 02,495 from PU wastes, become as for semihard and hard polyurethanes, in particular polyurethane foams, suitable described.

The Recyclatpolyole prepared after the mentioned methods contains the amines likewise resultant with the Glykolyse, which are health-endangering and in each case itself in addition disturbing in the PU systems formulated from the Recyclatpolyolen affect. They accelerate the reaction of the PU formation strong, form rigid groups of urea and decrease the controllability of the PU education reaction by other catalysts. Further that leads content at free amines in polyol components of PU systems in the contact with isocyanates immediately to high-thixotropic masses, as the patent specification DD-A-156 480 teaches.

On the field of the Entaminierung series of various methods known became. In accordance with DE-A-40 an acid number of significant over 1 mg KOH/g exhibits 24,601 Recyclatpolyol entaminierte by addition of monomerer acrylic acid, which can lead the Recyclatpolyol contained PU systems to difficulties into that. Further the significant odor disturbs after acrylic acid. After DE-A-44 16,322 can become also low molecular ureas and/or Carbamidsäureester the Entaminierung used. In EP-A-0 592,952 the use from Glycidethern becomes to the production of amine-poor Recyclatpolyolen described.

The so obtained Recyclatpolyole becomes used for the production of semihard and hard polyurethane foams. An improvement of the quality of the polyurethane foams by the use of these Recyclatpolyole is not apparent from the writings. Only DE-A-44 11,864 describes that by the use of Recyclatpolyol, prepared by Glykolyse of soft foam wastes using Glycidethern, hard polyurethane foams with elevated portion of open cells and reduced shrink prepared to become to be able.

To tough reading tables polyurethan-integral-foam materials become concerning the mechanical properties high demands provided. Beside the formation it applies for certain cell structures to achieve a fastidious mechanical quality level of the foams. Particularly it depends thereby on as high tear strength, elongation at break and a tensile strength as possible, in particular if, how for example with beer barrel casings the case is, strong external forces affect the polyurethane material.

The instant invention was therefore the basis the object, a simple and inexpensive method to the production tear strength improved by tough reading tables polyurethan-integral-foam materials with to develop elongation at break and tensile strength.

Surprisingly it was found that this object can become dissolved by the fact that becomes used with the production tough reading tables of the polyurethan-integral-foam materials a Recyclatpolyol, to which from Glykolyse of tough reading tables polyurethan-integral-foam materials using Glycidethern results.

Subject-matter of the invention is therefore a method to the production tear strength, elongation at break and tensile strength improved by tough reading tables polyurethan-integral-foam materials with by conversion of

a) organic and/or modified organic polyisocyanates also  
b) at least a high-molecular compound with at least two reactive hydrogen atoms and if necessary  
c) low molecular chain extension and/or crosslinking agents  
in presence of  
d) Catalysts,  
e) if necessary blowing agents  
f) as well as if necessary other aids and/or additives,  
by it the characterized is that as component b) at least a Recyclatpolyol, to which from Glykolyse of tough reading tables polyurethan-integral-foam materials using Glycidethern results, used becomes.

Subject-matters of the invention are further after this method prepared tough reading tables polyurethan-integral-foam materials as well as their use as beer barrel casing.

It was surprising and in no manner foreseeable that with use of Recyclatpolyolen prepared from tough reading tables polyurethan-integral-foam materials by Glykolyse again high-quality tough reading tables of polyurethan-integral-foam materials develop, which exhibit an improved tear strength, elongation at break and a tensile strength. It had to be expected rather that with use of Recyclatpolyolen the mechanical properties of the foam would worsen.

An economical process was thus found to the production by tough reading tables polyurethan-integral-foam materials, which are suitable excellent for the beer barrel casing.

As high-molecular compounds with at least two reactive hydrogen atoms completely according to invention or partial Recyclatpolyole becomes alone or used with one another in the mixture. Favourable way Recyclatpolyole in a portion of at least 30 Gew become the achievement of the desired mechanical characteristics. - %, related to the total amount of the component b), used. From economic reasons the use of the Recyclatpolyole substantial over 30 Gew can. - % lie and/or. the component b) complete of Recyclatpolyol consist. Natural ones know also less than 30 Gew. - % Recyclatpolyole used become.

The Recyclatpolyole becomes by Glykolyse of tough reading tables polyurethan-integral-foam materials, in particular their wastes, with kurzkettigen, hydroxylgruppenhaltigen compounds, like e.g. Ethylene glycol, diethylene glycol, triethylene glycol, Oligoethylenglykole, propylene glycol, dipropylene glycol, tri propylene glycol, Oligopropylenglykole, Butandiole, Neopentylglykol, Glycerol, ethanolamine, Diethanolamin and triethanolamine, if necessary in presence of catalysts, as for example alkali metal salts of kurzkettiger fatty acids, titanates, Stannaten and antimonates, with higher temperatures obtained.

When tough reading tables of polyurethan-integral-foam materials become in particular PU wastes used, as they for example particularly result with the production of beer barrel casings, whereby these can contain among other things fillers or reinforcing agents, which do not disturb the method.

The Recyclatpolyole which can be used according to invention is preferably amine-poor. They are in particular available by the fact that the Glykolyse of the polyurethan-integral-foam materials becomes in the manner conducted that over the entire course of the reaction mono and/or difunktionelle Glycidether is metered, as it is in EP-A-0 592,952 described.

With the production of the Recyclatpolyole commercial Glycidether is more insertable, which contains or two epoxy groups in the molecule.

As particularly suitable proved the monofunctional Glycidether of the general formula (I)

EMI5.1

in R = Phenyl, cyclohexyl, methylcyclohexyl, benzyle, i-Propyl, i-Butyl or methyl and/or ethyl-branched hydrocarbon chains with 5 to 10 C-atoms in the straight chain and/or a group of the general formula

EMI5.2

where A is an alkyl radical with 1 to 8 carbon atoms, n the values 3 to 12 and m the values 1 to 6 to assume can, meant.

Preferred used becomes 2-Ethylhexylglycidether or a mixture out

50 to 85 Gew. - % 2-Ethylhexylglycidether,  
10 to 35 Gew. - % or several compounds of the structure

EMI6.1

and

5 to 20 Gew. - % or several compounds of the structure

EMI6.2

whereby A is an alkyl radical with 1 to 8 carbon atoms, n the values 3 to 12 and m the values 2 to 6 assumed can. This Glycidylethergemisch can do prepared in known manner from 2-Ethylhexanol and epichlorohydrin, like it with the synthesis of 2-Ethylhexylglycidether results, and as technical crude product, only of inorganic ingredients freed, i.e. become without engagement of a distillation step, used.

As suitable further the difunktionellen Glycidether of the general formula proved

EMI6.3

in the R' = Diphenylmethylen, 2,2-Diphenylpropylen (bisphenol A), unbranched hydrocarbon chains with 4 to 10 C-atoms or methyl and/or ethyl-branched hydrocarbon chains with 4 to 8 C-atoms in the straight chain means.

As Glycidether monofunktional Glycidether of the general formula (I) can become alone or in mixture with one another, difunktionelle Glycidether of the general formula (II) alone or in mixture with one another or mixtures of single or several mono and difunktionellen Glycidethern used.

The reaction temperature becomes usually adjusted between 180 DEG C and 250 DEG C, preferably between 200 DEG C and 235 DEG C.

The reaction time is in dependence of the cross-linking-dense of the used polyurethanes and/or Polyharnstoffpolyurethane generally about 2 to 6 hours, preferably to 3 to 5 hours.

Favourable way the Glycidether becomes over the entire reaction time, preferably uniform, from polyurethan-integral-foam materials and oh group contained compounds existing the approach in an amount from usually 5 Gew,% to 20 Gew,%, related to the entire beginning, added.

To the production of the polyurethan-integral-foam materials after the invention process find to tough reading tables, beside which described above Recyclatpolyolen, which actual known structure components use, to which in detail the subsequent is to be implemented:

a) As organic and/or modified organic polyisocyanates (A) preferably come the actual known aliphatic, cyclo-aliphatic, araliphatic and the aromatic multi-valued isocyanates into question.

In detail are exemplarily mentioned: Alkylendiisocyanat with 4 to 12 carbon atoms in the alkylene group, like 1,12-Dodecan-diisocyanat, 2-Ethyl-tetramethylen-diisocyanat-1,4, 2-Methyl-pentamethylen-diisocyanat-1,5, Tetramethylen-diisocyanat-1,4 and preferably Hexamethylen-diisocyanat-1,6; cyclo-aliphatic diisocyanates, like Cyclohexan-1,3 and -1,4-diisocyanat as well as arbitrary mixtures this isomers, 1-Isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexan (Isophoron diisocyanat), 2,4 - and 2,6-Hexahydrotoluylen-diisocyanat as well as the corresponding isomer mixtures, 4,4 ' - , 2.2 ' - and 2.4 ' - as well as Dicyclohexylmethan diisocyanat the corresponding isomer mixtures, and preferably aromatic and polyisocyanates, like e.g. 2,4 - and 2,6-Toluylen-diisocyanat and the corresponding isomer mixtures, 4,4 ' - , 2.4 ' - and 2.2 ' - and the corresponding isomer mixtures, mixtures from 4,4 ' - and 2.4 ' - Diphenylmethan diisocyanaten, Polyphenyl polymethylen polyisocyanate, mixtures from 4,4 ' - , 2.4 ' - and 2.2 ' Diphenylmethan diisocyanat - and Polyphenylpolymethylen polyisocyanaten (rawMDI) and mixtures from rawMDI Diphenylmethan diisocyanaten and Toluylen diisocyanaten. The organic and polyisocyanates can become of single or in form their mixtures used.

Frequent ones become also so called modified multi-valued isocyanates, i.e. Products, which become obtained by chemical conversion of organic and/or polyisocyanates, used. Exemplarily mentioned is ester, urea, Biuret, allophane RK, Carbodiimid, ISO cyanogen urate, Uretidion and/or urethane groups contained and/or Polyisocyanate. In detail comes for example into considerations: Urethane groups contained organic, preferably aromatic polyisocyanates with NCO maintained ones from 33,6 to 15 Gew,%, preferably from 31 to 21 Gew,%, related to the total weight, prepared for example by conversion with low molecular diols, Triolen, dialkyl glycols, tri alkyl glycols or polyoxyalkylene glycols with molecular weights to 6000, in particular 4,4 ' - Diphenylmethan diisocyanat, modified 4,4 ' - and 2,4 modified with molecular weights to 1500, ' - , or modified rawMDI or 2,4 Diphenylmethan diisocyanatmischungen - and/or. 2,6-Toluylen-diisocyanat, whereby as and/or. Polyoxyalkylene glycols, which are single or used as mixtures to become to be able, for example mentioned: Diethylen, dipropylene glycol, Polyoxyethylen, Polyoxypropylen and Polyoxypropylenpolyoxyethylen glycols, - triole and/or - tetrole. Suitable ones are also NCO groups of contained prepolymers with NCO maintained ones of 30 to 15 Gew,%, preferably from 28 to 20 Gew,%, related to the total weight, prepared from the subsequent described polyester and/or preferably polyether polyols and 4,4 ' - Diphenylmethan diisocyanat, mixtures from 2,4 ' - and 4,4 ' - Diphenylmethan diisocyanat, 2,4 - and/or 2,6-Toluylen-diisocyanaten or rawMDI. Bewährt has themselves furthermore liquid, Carbodiimidgruppen and/or ISO cyanogen urate rings of contained polyisocyanates with NCO maintained ones from 33,6 to 15, preferably 31 to 21 Gew,%, related to the total weight, e.g. on basis of 4,4 ' - , 2.4 ' - and/or 2.2 ' -

Diphenylmethan diisocyanat and/or 2,4 - and/or 2,6-Toluylen-diisocyanat.

The modified polyisocyanates can with one another or with unmodified organic polyisocyanates like e.g. 2,4 ' - , 4,4 ' - , rawMDI, 2,4 Diphenyl methane diisocyanat - and/or 2,6-Toluylen-diisocyanat mixed become if necessary.

Particularly preserved has itself as organic polyisocyanates aromatic polyisocyanates and to come therefore preferably to the application: RawMDI, mixtures out Toluylen diisocyanaten and rawMDI or mixtures from modified urethane groups contained organic polyisocyanates with a NCO content from 33,6 to 15 Gew. - %, in particular such on basis of Toluylen diisocyanaten, 4,4 ' - Diphenylmethan diisocyanat, Diphenylmethan diisocyanat isomer mixtures or rawMDI and in particular rawMDI with a Diphenylmethan diisocyanat Isomerengehalt from 30 to 80 Gew. - %, preferably from 30 to 55 Gew. - %.

b) As high-molecular compounds with at least two reactive hydrogen atoms the described above Recyclatpolyole used becomes according to invention. Besides other high-molecular compounds with at least two reactive hydrogen atoms can become (B) along-used. For this appropriately such come with a functionality from 2 to 8, preferably 2 to 6, and a molecular weight of 1000 to 8000, preferably from 1200 to 6000 into considerations. Preserved ones have themselves e.g. Polyether polyamine and/or preferably polyols selected from the group of the polyether polyols, polyester polyols, Polythioetherpolyole, polyesteramides, hydroxylgruppenhaltigen polyacetals and hydroxylgruppenhaltigen aliphatic polycarbonates or mixtures from at least two of the polyols mentioned. Preferably polyester polyols and/or polyether polyols find application. The hydroxyl number of the polyhydroxyl compounds preferably amounts to thereby in all rule 25 to 850 and 300 to 750.

Suitable polyester polyols know for example from organic dicarbonic acids with 2 to 12 carbon atoms, preferably aliphatic dicarboxylic acids with 4 to 6 carbon atoms, and multi-valued alcohols, preferably diols, with 2 to 12 carbon atoms, preferably 2 to 6 carbon atoms prepared become. As dicarbonic acids come for example into considerations: Succinic acid, glutaric acid, adipic acid, cork-acidic, azelaic acid, sebacic acid, Decandicarbonsäure, maleic acid, fumaric acid, phthalic acid, isophthalic acid and terephthalic acid. The dicarbonic acids can become thereby both single and in the mixture among themselves used. In place of the free dicarbonic acids also the corresponding dicarbonic acid derivatives can, like e.g. Dicarbonic acid esters of alcohols with 1 to 4 carbon atoms or dicarboxylic acid anhydrides used become. Preferably used becomes dicarbonic acid mixtures from amber, glow acre and adipic acid in proportions from for example 20 to 35: 35 to 50: 20 to 32 Gew. - Parts, and in particular adipic acid. Examples for zwei- und multi-valued alcohols, in particular diols are: Ethanediol, diethylene glycol, 1,2 - and/or. 1,3-Propandiol, dipropylene glycol, 1,4-Butandiol, 1,5-Pentandiol, 1,6-Hexandiol, 1,10-Decandiol, glycerol and trimethylolpropane. Preferably used becomes ethanediols, diethylene glycol, 1,4-Butandiol, 1,5-Pentandiol, 1,6-Hexandiol or mixtures from at least two of the diols mentioned, in particular mixtures from 1,4-Butandiol, 1,5-Pentandiol and 1,6-Hexandiol. Used one to become to be able furthermore polyester polyols from lactones, e.g. epsilon - caprolactone or hydroxycarboxylic acids, e.g. omega - Hydroxycaprionsäure.

To the production of the polyester polyols the organic can, e.g. aromatic and preferably aliphatic, polycarboxylic acids and/or - derivatives and multi-valued alcohols catalyst-free or preferably in presence of esterification catalysts, appropriately in an atmosphere from inert gas, like e.g. Nitrogen, carbon dioxide, helium, argon among other things, in which melt with temperatures from 150 to 250 DEG C, 180 to 220 DEG C bottom reduced pressure up to the desired acid number, which favourable-proves smaller as 10, preferably smaller as 2 is, is preferably polykondensiert if necessary. After a preferable embodiment the ester mixture is polykondensiert with the above temperatures up to an acid number from 80 to 30, preferably 40 to 30, bottom normal pressure and subsequent a bottom pressure of smaller as 500 mbar, preferably 50 to 150 mbar. As esterification catalysts come for example iron, cadmium, cobalt, lead, zinc, antimony, magnesium, titanium and tin catalysts in the form of metals, metal oxides or metal salts into considerations. The polycondensation can however also in liquid phase in presence of dilution and/or Schlepfmitteln, like e.g. Benzene, toluene, xylene or chlorobenzene, to the azeotropic Abdestillation of the condensation water conducted become.

The production of the polyester polyols the organic polycarboxylic acids become and/or - derivatives and multi-valued alcohols favourable-proves in the molar ratio from 1:1 to 1.8, preferably 1:1,05 to 1.2 polykondensiert.

The obtained polyester polyols possess preferably a functionality from 2 to 4, in particular 2 to 3, and a molecular weight of 480 to 3000, preferably 1200 to 3000 and in particular 1800 to 2500.

In particular as polyols used become however polyether polyols, after prior art processes, for example by anionic polymerization with alkali hydroxides, like z. B. Sodium or potassium hydroxide or alkali alcoholates, like z. B. Natriummethylat, sodium or Kaliumethylat or Kaliumisopropylat, as catalysts and bottom addition at least one starter molecule, which contains 2 to 8, preferably 2 to 6, reactive hydrogen atoms bonded, or by cationic polymerization with Lewis acidic ones, like Antimonpentachlorid, Borfluorid Etherat among other things or Bleicherde, when catalysts become from or several alkylene oxides with 2 to 4 carbon atoms in the alkylene group a prepared.

Suitable alkylene oxides are for example tetrahydrofurane, 1,3-Propylenoxid, 1,2 - and/or. 2,3-Butylenoxid, styrene oxide and preferably ethylene oxide and 1,2-Propylenoxid. The alkylene oxides can become single, alternate successively or as mixtures used. As starter molecules come for example into considerations: Water, organic dicarbonic acids, like succinic acid, adipic acid, phthalic acid and terephthalic acid, aliphatic and aromatic, if necessary N-mono, N, n and N, N' dialkyl-substituted diamines with 1 to 4 carbon atoms in the alkyl radical, like if necessary mono and dialkyl-substituted ethyl diamine, diethylenetriamine, triethylenetetramine, 1,3-Propylendiamin, 1,3 - and/or. 1,4-Butylendiamin, 1,2, 1,3, 1,4, 1.5 - and 1,6-Hexamethylendiamin, phenylene diamines, 2,3, 2,4 - and 2,6-Toluylendiamin and 4,4 ' - , 2,4 ' - and 2,2 ' - Diamino diphenylmethan.

Furthermore as starter molecules come into considerations: Alkanolamines, like e.g. Ethanolamine, N-methyl and N-ethyl-ethanolamin, Dialkanolamine, like e.g. Diethanolamin, N-methyl and N-ethyl-diethanolamin, and Trialkanolamine, like e.g. Triethanolamine, and ammonia. Preferably used becomes multi-valued, in particular two and/or trivalent alcohols, like ethanediols, Propandiol-1,2 and -1,3, diethylene glycol, dipropylene glycol, Butandiol-1,4, Hexandiol-1,6, glycerol, trimethylolpropane, pentaerythritol, sorbitol and sucrose.

The polyether polyols, preferably Polyoxypolypropylen and Polyoxypolypropylen polyoxyethylene polyole, possess a functionality from preferably 2 to 6 and in particular 2 to 4 and molecular weights of 1000 to 8000, preferably 1200 to 6000 and in particular 1800 to 4000 and suitable Polyoxypolytetramethyleneglycol a molecular weight to approximate 3500.

As polyether polyols furthermore polymere-modified polyether polyols, preferably graft polyether polyole, in particular such on styrene and/or acrylonitrile basis, are suitable those through in situ polymerization of acrylonitrile, styrene or preferably mixtures from styrene and acrylonitrile, e.g. in the weight ratio 90: 10 to 10: 90, preferably 70: 30 to 30: 70 in appropriately the aforementioned polyether polyols the analogous indications of the German patent specifications 11 11 394, 12 22 669 (US 3,304,273, 3,383,351, 3,523,093), 11 52 536 (GB 10 40 452) and 11 52 537 (GB 987,618) prepared Polyether will polydispersionen, as well as, those as disperse phase, usually in an amount from 1 to 50 Gew.%, contain preferably 2 to 25 Gew.%, e.g. polyureae, Polyhydrazide, third. - Amino group of bonded contained polyurethanes and/or melamine and e.g. described become in the EP-B-011 752 (US 4,304,708), US 4,374,209 and DE-A-32 31,497.

The polyether polyols can become just like the polyester polyols single or in the form of mixtures used. Furthermore they can graft polyether polyol with that or become polyester polyols as well as the hydroxylgruppenhaltigen polyesteramides, polyacetals, polycarbonates and/or Polyetherpolyaminen mixed.

As hydroxylgruppenhaltige polyacetals e.g. come. the compounds in question, producible from glycols, like diethylene glycol, triethylene glycol, 4,4' - Dihydroxyethoxy diphenyl dimethylmethan, hexanediols and formaldehyde. Also by polymerization of cyclic acetals suitable polyacetals can be manufactured.

As hydroxyl groups exhibiting polycarbonates come such the actual known type into consideration, those for example by conversion of diols, like Propandiol (1,3), Butandiol (1,4) and/or Hexandiol (1,6), diethylene glycol, triethylene glycol or tetraethylene glycol with diaryl carbonates, e.g. Diphenyl carbonate, or phosgene prepared to become to be able.

Among the polyesteramides e.g. rank. the out multi-valued, satisfied and/or unsaturated carbonic acids and/or. their anhydrides and multi-valued satisfied and/or unsaturated Aminoalkoholen or mixtures from multi-valued alcohols and Aminoalkoholen and/or polyamines of recovered, predominantly linear condensates.

Suitable Polyetherpolyamine can become from the above polyether polyols after prior art processes prepared. Exemplarily mentioned is the Cyanoalkylierung of Polyoxyalkylen polyol and subsequent hydrogenation of the formed nitrile (US 3,267,050) or the partial or complete amination of Polyoxyalkylen polyol with amines or ammonia in presence of hydrogen and catalysts (DE 12 15 373).

c) The elastic polyurethan-integral-foam materials can become without or bottom use of chain extension and/or crosslinking agents (C) prepared. To the modification of the mechanical properties, e.g. , however the addition of chain extenders, crosslinking agents or if necessary also mixtures can prove to the hardness of it as favourable. As chain extension and/or crosslinking agents used become diols and/or Triole with molecular weights smaller as 400, preferably from 60 to 300. Into considerations for example aliphatic, cyclo-aliphatic and/or araliphatic diols with 2 to 14, preferably 4 to 10 carbon atoms come, like e.g. Ethylene glycol, Propandiol-1,3, Decandiol-1,10, o, m, p-Dihydroxycyclohexan, diethylene glycol, dipropylene glycol and preferably Butandiol-1,4, Hexandiol-1,6 and until (2-hydroxy-ethyl) - hydrochinon, Triole, like 1,2,4, 1,3,5-Trihydroxy-cyclohexan, glycerol and trimethylolpropane and low molecular hydroxylgruppenhaltige polyalkylene oxides on basis ethyl and/or 1,2-Propylenoxid and the aforementioned diols and/or Triolen as starter molecules.

If to the production of the polyurethan-integral-foam materials chain extenders, crosslinking agents or mixtures of it find application, these come appropriately in an amount from 0 to 20 Gew. - %, preferably from 2 to 8 Gew. - %, related to the weight of the polyol compound (B) to the use.

d) When catalysts (D) become the production tough reading tables of the polyurethan-integral-foam materials in particular compounds used, which the reaction of the reactive hydrogen atoms, in particular hydroxyl groups, contained compounds of the component (B) and (C) with organic, if necessary modified polyisocyanates (A) strong to accelerate if necessary. Into considerations organic metal compounds, preferably organic tin compounds, come like tin (II) - salt from organic carbonic acids, e.g. tin (II) - acetate, tin (II) - octoat, tin (II) - and tin (II) ethylhexoat - laurat and the dialkyl tin (IV) - salts from organic carbonic acids, e.g. , dibutyltin dilaurate, Dibutylzinmaleat Dibutyl zinndiacetat and Dioctylzinndiacetat. The organic metal compounds become alone or preferably used in combination with strong basic amines. Mentioned ones are for example amidines, like 2,3-Dimethyl-3,4,5,6-tetrahydropyrimidin, tertiary amines, like triethylamine, tributylamine, dimethylbenzylamine, N-methyl, N-ethyl, N-Cyclohexylmorpholin, N, N, N', N' tetramethylethylenediamine, N, N, N', N' Tetramethyl butandiamin, N, N, N', N' Tetramethyl-hexandiamin-1,6, Pentamethyl diethylenetriamin, Tetramethyl more diaminoethylether, until (dimethylaminopropyl) - urea, Dimethylpiperazin, 1,2-Dimethyl-imidazol, 1-Aza-bicyclo (3,3,0) - octan and preferably 1,4-Diaza-bi-cyclo (2,2,2) - octan, and Alkanolaminverbindungen, like triethanolamine, tri isopropanol amine, N-methyl and N-ethyl-diethanolamin and dimethylethanolamine.

Furthermore as catalysts come into considerations: Trichloroethylene (dialkylaminoalkyl) - s-hexahydrotriazine, in

particular trichloroethylene (N, N-dimethylaminopropyl) - s-hexahydrotriazin, tetraalkyl ammonium hydroxides, like tetramethylammonium hydroxide, alkali hydroxides, like sodium hydroxide and alkali alcoholates, like Natriummethylat and Kaliumisopropylat, as well as alkali salts of langkettigen fatty acids with 10 to 20 C-atoms and if necessary sidecontinuous oh group. Preferably used becomes 0.001 to 5 Gew. - %, in particular 0.05 to 2 Gew. - %, catalyst and/or. Catalyst combination, related to the weight of the component (B).

e) To blowing agents (E), which belongs to used the production of the polyurethan-integral-foam materials if necessary to become to be able, preferably waters, with isocyanate groups bottom formation of carbon dioxide responsive. The amounts of water, which become appropriately used, amount to 0.1 to 8 Gew. - Parts, preferably 1.5 to 5.0 Gew parts and in particular 0.5 to 2.0 Gew. - Parts, related to 100 Gew. - Parts the Polyoxyalkylen polyole.

In the mixture with water also physical acting blowing agents can become used. Suitable ones are liquids, which are inert opposite organic, if necessary modified polyisocyanates (C) and boiling points of bottom 100 DEG C, preferably bottom 50 DEG C exhibit, in particular between -50 DEG C and 30 DEG C with atmospheric pressure, so that they evaporate the bottom influence of the exothermic polyaddition reaction. Examples of such, preferably useful liquids are alkanes, like heptane, hexane, n and ISO pentane, preferably technical mixtures from n and ISO pentanes, n and ISO butane and propane, cycloalkanes, like cyclopentane and/or cyclohexane, ether, like Furan, dimethyl ethers and diethyl ether, Ketone, like acetone and methyl ethyl ketone, carbonic acid alkyl ester, like methyl formate, Dimethyloxalat and ethyl acetate and halogenated hydrocarbons, like methylene chloride, Dichlormonofluormethan, difluoromethane, tri fluorine methane, Difluorethan, tetrafluoroethane, chlorine difluorethan, 1,1-Dichlor-2,2,2-trifluorethan, 2,2-Dichlor-2-fluorethan and heptafluoropropane. Also mixtures of these low liquids among themselves and/or with other substituted or unsubstituted hydrocarbons can become used. Furthermore suitable ones are e.g. organic carbonic acids, like. formic acid, acetic acid, oxalic acid, Ricinolsäure and carboxylgruppenhaltige compounds.

Preferably find use waters, chlorodifluoromethane, Chlordifluorethan, Dichlorfluorethan, pentane mixtures, cyclohexane and mixtures from at least two of these blowing agents, e.g. Mixtures from water and cyclohexane, mixtures from chlorodifluoromethane and 1-Chlor-2,2-difluorethan and if necessary waters.

f) The reaction mixture to the production tough reading tables of polyurethan-integral-foam materials also still conventional aids and/or additives (f) can become the incorporated if necessary in PU chemistry. Mentioned ones are for example foam stabilisers, fillers, dyes, pigments, flame retardant, hydrolysis protective agent, fungistatische and bakteriostatisch acting substances.

As fillers, in particular strengthening acting fillers, are the actual known, conventional organic and inorganic fillers, reinforcing agent, loading means, agent to the improvement of the abrasion behavior in paints, coating agent etc. to understand. In detail are exemplarily mentioned: inorganic fillers like silikatische minerals, for example layer silicates such as Antigorit, Serpentin, horn screens, amphiboles, Chrisotil, talcum powder; Metal oxides, like kaolin, aluminas, titanium oxides and iron oxides, metal salts such as chalk, heavy-late and inorganic pigments, like cadmium sulfide, zinc sulfide as well as glass among other things. Preferably used becomes kaolin (China Clay), aluminium silicate and Copräzipitate from barium sulfate and aluminium silicate as well as natural and synthetic fibrous minerals such as wollastonite, metal and in particular glass fibers various length, which can be smoothed if necessary. As organic fillers come for example into considerations: Coal, melamine, Kollophonium, Cyclopentadienylharze and graft polymers as well as cellulose fibers, PP, Polyacrylnitril, PU, polyester fibers on the basis of aromatic and/or aliphatic dicarbonic acid esters and in particular carbon fibers.

Suitable flame retardants are for example Trikresylphosphat, trichloroethylene (2-chlorethyl) phosphate, trichloroethylene (2-chlorpropyl) phosphate, trichloroethylene (1,3-dichlorpropyl) phosphate, trichloroethylene (2,3-dibrompropyl) phosphate, Tetrakis (2-chlorethyl) - ethylendiphosphat, Dimethylmethanphosphonat, Diethanolaminomethylphosphonsäurediethylester as well as commercial halogenhaltige Flammenschutzpolyole. Except the halogeneous-substituted phosphates specified already also inorganic or organic flame retardants, like red phosphorus, can alumina hydrate, antimony trioxide, arsenic oxide, ammonium polyphosphate and calcium sulfate, blowing graphite or Cyanursäurederivate, like e.g. Melamine, or mixtures from at least two flame retardants, as. ammonium polyphosphates and melamine as well as corn starch or ammonium polyphosphate, melamine and blowing graphite and/or aromatic polyesters the flaming fastening of the polyisocyanate polyaddition products used if necessary if necessary become e.g. Generally it proved as convenient, to 5 to 50 Gew. - Parts, preferably 5 to 25 Gew. - Parts, the flame retardants mentioned for in each case 100 Gew. - To use parts of the component (B).

Closer indications over specified other conventional auxiliary and additives the above are the technical literature, for example the Monographie of J.H. Saunders and K.C. Fresh "High of polymer" tape XVI, PU, part 1 and 2, publishing house Interscience Publishers 1962 and/or. 1964, or the plastic handbook, polyurethanes, tape VII, Hans he publishing house, Munich, Vienna, 1. , 2. and 3. Edition, 1966, to take from 1983 and 1993.

The production tough reading tables of the polyurethan-integral-foam materials the organic polyisocyanates (A), high-molecular compounds with at least two reactive hydrogen atoms (B) and if necessary chain extension and/or crosslinking agent (C) in such amounts the conversion brought become that the equivalence ratio of NCO groups of the polyisocyanates (A) amounts to preferably to the sum of the reactive hydrogen atoms of the components (B) and (C) 0.9 to 1,15:1 if necessary.

Tough reading tables the polyurethan-integral-foam materials favourable-proves free-foamed after that one SHOT methods or Prepolymerverfahren with the help of high pressure or low-pressure technique in open or closed forming tools, for example metallic forming tools, or (local foam) prepared. When particularly favourably has it proven, to work after the two-component method and the structure components (B), (D) and if necessary (C) to combine (E) and (f) in the

component (A) and to use as component (B) the organic and/or modified organic polyisocyanates (A) or mixtures from the polyisocyanates and if necessary blowing agent mentioned (D).

The starting components become mixed with a temperature from 15 to 90 DEG C, preferably from 20 to 60 DEG C and in particular from 20 to 35 DEG C, and in case of the production of form foam materials into the open or into the closed forming tool introduced. The forming tool temperature amounts to appropriately 20 to 110 DEG C, preferably 30 to 60 DEG C and in particular 45 to 50 DEG C.

After the invention process to prepared tough reading tables of polyurethan-integral-foam materials point a density from 600 to 1,100 kg/m<sup>3</sup>, preferably from 700 to 800 kg/m<sup>3</sup> up. They have a cellular core and a densified edge zone.

To tough reading tables according to invention the polyurethan-integral-foam materials point

a tear strength of at least 22 N/mm, preferably from 22 to 26 N/mm, certain according to DIN 53507, an elongation at break of at least 27%, preferably from 27 to 50%, certain according to DIN 53504, and a tensile strength of at least 6.8 N/mm<sup>2</sup>, preferably of 6,8 to 8.0 N/mm<sup>2</sup>, certain according to DIN 53504, up.

After the invention process prepared tough reading tables polyurethan-integral-foam materials are for all applications suitable conventional for tough reading tables polyurethan-integral-foam materials. Used in particular become them for beer barrel casings.

The invention becomes more near explained in the subsequent embodiments.

Example 1 (comparison example):

A-component

Mixture out:

63,51 Gew. - Parts of a Polyoxypropylen polyoxyethylen polyole with the OHZ 35 mg KOH/g, started with Glycerol,  
9,6 Gew. - Parts of a Polyoxypropylen polyoxyethylen polyole with the OHZ 29 mg KOH/g, started with propylene glycol,  
17,95 Gew. - Parts ethyl diamine of a started Polyoxypropylenpolyols with the OHZ 740 mg KOH/g,  
0,98 Gew. - Parts 33 gew. - %igen solution of Dabco in dipropylene glycol,  
4,86 Gew. - Parts of trichloroethylene (2-Chlorisopropyl) phosphate (TCPP),  
0,5 Gew. - Parts waters and  
2,60 Gew. - Parts colouring paste

B-component:

Urethane groups contained Prepolymers with a NCO content of 28%, prepared by conversion of diphenylmethane diisocyanate/polyisocyanate with a propylene glycol started Polyoxypropylen polyole with the OHZ 250 mg KOH/g.

100 Gew. - Parts of the A-component became with 53 Gew. - An tough-elastic integral foam material with the subsequent characteristics developed for parts of the B-component reacted and:

<tb>< TABLE> Columns=2	
<tb> bulk density moulding [kg/m <sup>3</sup> ]:	<September> 710
<tb> hardness [shore D]:	<September> 40
<tb> tensile strength [N/mm <sup>2</sup> ]:	<September> 6,6
<tb> elongation at break [%]:	<September> 26,9
<tb> tear strength [N/mm]:	<September> 21,1
<tb>< /TABLE>	

Example 2 (production of the Recyclatpolyols)

2000 g tough reading tables of an integral foam waste (beer barrel casing) diethylene glycol (DEG) and 0.1 Gew became with 205 DEG C into a mixture from 1000 g. - % itoctoat (related to DEG and PU waste) in such a way registered that piston contents remained agitatable. Bottom agitations this temperature 2.5 h was maintained. During the reaction time 12 Gew became. - % 2-Ethylhexylglycidether (related to amount DEG and PU waste) uniform meters.

Subsequent one became cooled on 150 DEG C, 3 Gew. - % 2-Ethylhexylglycidether meters and with this temperature 0.5 h driven. It became an homogeneous black liquid with the subsequent characteristics obtained:



<tb>< TABLE> Columns=2
<tb> OHZ< September> 370 mg KOH/g
<tb> sp< September>< 0.1 mg KOH/g
<tb> viscosity< September> 5280 mPa.s
<tb> MDA content< September>< 0,1 %
<tb>< /TABLE>

### Example 3

#### A-component

##### Mixture out:

30 Gew. - Parts Recyclatpolyol, prepared in accordance with example 2 from integral foam material wastes (beer barrel casings) with the OHZ 370 mg KOH/g,  
 52,40 Gew. - Parts of a Polyoxypropylen polyoxyethylen polyole with the OHZ 35 mg KOH/g, started with Glycerol,  
 10,20 Gew. - Parts of a Polyoxypropylen polyoxyethylen polyole with the OHZ 29 mg KOH/g, started with propylene glycol,  
 6,0 Gew. - Parts ethyl diamine of a started Polyoxypropylenpolyols with the OHZ 740 mg KOH/g,  
 0,90 Gew. - Parts 33 gew. - %igen solution of Dabco in dipropylene glycol and  
 0,5 Gew. - Parts waters.

#### B-component: analogous example 1

100 Gew. - Parts of the A-component became with 57,3 Gew. - An tough-elastic integral foam material with the subsequent characteristics developed for parts of the B-component reacted and:

<tb>< TABLE> Columns=2
<tb> bulk density moulding [kg/m< 3>]: <September> 730
<tb> hardness [shore D]: <September> 39
<tb> tensile strength [N/mm< 2>]: <September> 7,9
<tb> elongation at break [%]: <September> 32,4
<tb> tear strength [N/mm]: <September> 25,1
<tb>< /TABLE>

### Example 4

#### A-component

##### Mixture out:

39 Gew. - Parts Recyclatpolyol, prepared in accordance with example 2 from integral foam material wastes (beer barrel casings) with the OHZ 370 mg KOH/g,  
 48,9 Gew. - Parts of a Polyoxypropylen polyoxyethylen polyole with the OHZ 35 mg KOH/g, started with Glycerol,  
 10,7 Gew. - Parts of a Polyoxypropylen polyoxyethylen polyole with the OHZ 29 mg KOH/g, 0.9 Gew, started with propylene glycol. - Parts 33 gew. - %igen solution of Dabco in dipropylene glycol and  
 0,5 Gew. - Parts waters.

#### B-component: analogous example 1

100 Gew. - Parts of the A-component became with 54 Gew. - An tough-elastic integral foam material with the subsequent characteristics developed for parts of the B-component reacted and:

<tb>< TABLE> Columns=2
<tb> bulk density moulding [kg/m< 3>]: <September> 700
<tb> hardness [shore D]: <September> 41
<tb> tensile strength [N/mm< 2>]: <September> 7,0
<tb> elongation at break [%]: <September> 49,6
<tb> tear strength [N/mm]: <September> 23,8
<tb>< /TABLE>



## Result Page

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1. Method to the production by tough reading tables polyurethan-integral-foam materials with improved tear strength, elongation at break and tensile strength by conversion of

- a) organic and/or modified organic polyisocyanates also
  - b) at least a high-molecular compound with at least two reactive hydrogen atoms and if necessary
  - c) low molecular chain extension and/or crosslinking agents
  - in presence of
  - d) Catalysts,
  - e) if necessary blowing agents
  - f) as well as if necessary other aids and/or additives,
- characterised in that as component b) at least a Recyclatpolyol, to which from Glykolyse of tough reading tables polyurethan-integral-foam materials using Glycidethern results, used becomes.

2. Verfahren according to claim 1, characterised in that the Recyclatpolyol in a portion of at least 30 Gew. - becomes %, related to the total amount of the component b), used.

3. Process according to claim 1 or 2, characterised in that with the production of the Recyclatpolyole mono and/or difunktionelle Glycidether used becomes.

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4. Process according to one of claims 1 to 3, characterised in that the used Recyclatpolyol is amine-poor.

5. Zähelastische of polyurethan-integral-foam materials with improved tear strength, elongation at break and tensile strength, available by conversion of

- a) organic and/or modified organic polyisocyanates also
  - b) at least a high-molecular compound with at least two reactive hydrogen atoms and if necessary
  - c) low molecular chain extension and/or crosslinking agents
  - in presence of
  - d) Catalysts,
  - e) if necessary blowing agents
  - f) as well as if necessary other aids and/or additives,
- characterised in that as component b) at least a Recyclatpolyol, to which from Glykolyse of tough reading tables polyurethan-integral-foam materials using Glycidethern results, used becomes.

6. Zähelastische of polyurethan-integral-foam materials according to claim 5 characterised in that the Recyclatpolyol in a portion of at least 30 Gew. - becomes %, related to the total amount of the component b), used.

7. Tough reading tables of polyurethan-integral-foam materials after one of the claims 5 or 6, characterised in that the foams a tear strength of at least 22 N/mm < 2 > exhibit.

8. Tough reading tables of polyurethan-integral-foam materials after one of the claims 5 or 6, characterised in that the foams an elongation at break of at least 27% exhibit.

9. Tough reading tables of polyurethan-integral-foam materials after one of the claims 5 or 6, characterised in that the foams a tensile strength of at least 6.8 N/mm < 2 > exhibit.

10. Use tough reading tables of the polyurethan-integral-foam materials in accordance with one of the claims 5 to 9 as beer barrel casing.